DEVELOPMENT OF MIXED MATRIX SULFONATED POLYSULFONE AND POLYETHERSULFONE FOR PROTON EXCHANGE MEMBRANE FUEL CELL APPLICATION

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Date : ....

To my beloved father and mother, Mr Rosman Darus and Madam Noraini Ghazali

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ABSTRACT

The objective of this study was to prepare a mixed matrix of sulfonated polysulfone (SPSU) and polyethersulfone (PES) and investigate its potential for proton exchange membrane fuel cell (PEMFC) application. Four samples were prepared in this study, a sample of PSU/PES as a reference and 3 other samples SPSU/PES with the amount of sulfonating agent (trimethylsilyl chlorosulfonate, TMSCS) varied for each sample (10mL, 15mL and 20mL). The sulfonated membrane samples (SPSU/PES 1, SPSU/PES 2 and SPSU/PES 3) were prepared in 20 hours stirring time, 10 minutes of TMSCS dropwise time and 15 minutes of sodium methoxide dropwise time. FTIR test confirmed that the sulfonation process was successful for all three sulfonated samples where wavelength of 1029.27 cm^{-1} detected for sample SPSU/PES 1, 1035.75 cm^{-1} for sample SPSU/PES 2 and 1031.52 cm^{-1} for sample SPSU/PES 3. Referring to water/methanol mixture uptake test, sample SPSU/PES 3 had the highest swelling degree with the amount of 62.93% followed by SPSU/PES 2 (58.95%), SPSU/PES 1 (46.9%) and PSU/PES (33.43%). Elemental analysis was done in order to obtain data for degree of sulfonation calculation. From the calculation, it was found that sample SPSU/PES 3 has the highest degree of sulfonation (72.53%) followed by SPSU/PES 2 (55.49%) and SPSU/PES 1 (38.46%).

ABSTRAK

Objektif tesis ini ialah untuk menyediakan matriks bercampur sulfonated polysulfone (SPSU) dan polyethersulfone (PES) dan mengkaji potensinya untuk aplikasi sel bahan api penukaran proton.Empat sampel telah disediakan dalam proses tesis ini dengan satu sampel PSU/PES sebagai rujukan dan 3 sampel SPSU/PES yang mengandungi kandungan ejen sulfonan trimethylsilyl chlorosulfonate, TMSCS) yang berlainan (10mL, 15mL and 20mL). Sampel mebran tersulfon (SPSU/PES 1, SPSU/PES 2 and SPSU/PES 3) telah disediakan dalam 20 jam masa kacauan, 10 minit masa titisan TMSCS dan 15 minit masa titisan natrium metokisida. Ujian FTIR mengesahkan bahawa proses sulfonasi bagi ketiga-tiga sampel SPSU/PES telah berjaya di mana panjang gelombang 1029.27 cm^{-1} dikesan pada sampel SPSU/PES 1, 1035.75 cm^{-1} untuk sampel SPSU/PES 2 dan 1031.52 cm^{-1} for sampel SPSU/PES 3. Merujuk kepada ujian pengambilan campuran air/methanol, sampel SPSU/PES 3 mempunyai darjah pembengkakan yan tertinggi dengan jumlah 62.93% diikuti oleh SPSU/PES 2 (58.95%), SPSU/PES 1 (46.9%) dan PSU/PES (33.43%). Analisis elemen telah dijalankan untuk mendapatkan data bagi pengiraan darjah pengsulfonan. Daripada pengiraan, didapati bahawa sampel SPSU/PES 3 mempunyai darjah pengsulfonan yang tertinggi (72.53%) diikuti oleh SPSU/PES 2 (55.49%) dan SPSU/PES 1 (38.46%).

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CHAPTER I

INTRODUCTION

1.1 Background of Study

Power generation with fewer hazards to environment has been a major world concern nowadays. The environmental concern has been a serious issue due to the reducing thickness of the ozone layers and increasing number of global warming and green house effects cases. Scientists, engineers and researchers have been starting to search for alternative fuels that can replace the world's dependency on fossil fuels such as petroleum and natural gas. Most of vehicles in the world nowadays use gasoline and diesel as their fuel. The usage of these types of hydrocarbon will contribute massive amount of pollutants from the effluents of the fuel conversion process.

Although several new inventions had been created in order to reduce the pollution made by gasoline and diesel powered engines such as replacing two strokes engine with four strokes engine for motorcycles and integrating the hybrid electric and fuel system into car engines, the demand for a cleaner, more energy efficient fuel will not stop there as the amount of fossil fuel is decreasing day by day and the price is going sky high per year. This particular matter has encouraged the research in various aspects for fuel cell. Fossil fuel savings, higher energy conversion efficiency, low pollution and noise level and affordable maintenance costs has made fuel cells are the most competitive type among other energy conversion devices (Smitha *et al*, 2005).

Major countries such as United States, Canada, United Kingdom and Japan are currently competing for the fuel cell application in various fields especially transportation and stationary power generation. The Japanese advance in technologies has made them the leading force for fuel cell implementation among other emerging Asian countries.

Malaysia is set to undertake the fuel cell technology application when ETI Tech (M) Sdn Bhd, a local leading energy solutions provider announced its smart partnership with P21 GmbH, a world class Munich-based international developer and manufacturer of efficient fuel cell powered Uninterrupted Power Supply (UPS) power system in 2006. This partnership is expected to revolutionize the applications of existing conventional high power backup systems. Due to this pioneering step, Malaysia can be considered ready to adapt with the fuel cell implementation in industrial and local applications in the near future.

Due to the environmental concern and decreasing amount of fossil fuels, fuel cell has been introduced to the commercial application. Transportation field has been the medium for fuel cell technology implementation. Smart cars were being developed by major vehicles companies such as General Motors, Toyota, Honda and Nissan to possibly replace conventional fossil fuel powered engine vehicles in the future. Smart cars use PEMFC to convert the fuel (mostly hydrogen) into electrical energy which is used as the car's power source.

Worldwide fuel cell-related sales increased by 41% between 2002 and 2003, according to the first worldwide fuel cell industry survey conducted by Pricewaterhouse Coopers for the US Fuel Cell Council, the national trade association for the fuel cell industry. The world fuel cell demand is expected to reach US$ 2.6 billion in 2009. Total commercial fuel cell demand in 2004 totaled $375 million and is anticipated to grow to $2,580 million by 2009. This anticipated figure includes revenues associated with prototyping and test marketing activities. By 2014, the forecasted growth should reach $13.6 billion. World fuel cell spending (including research and development funding and investment in fuel cell enterprises, in addition to commercial sales) will more than double to $10.8 billion in 2009 (Shirley and Donald Georgi, 2005). Figure 1.1 shows the world's fuel cell demand growth from 2004 to 2009.

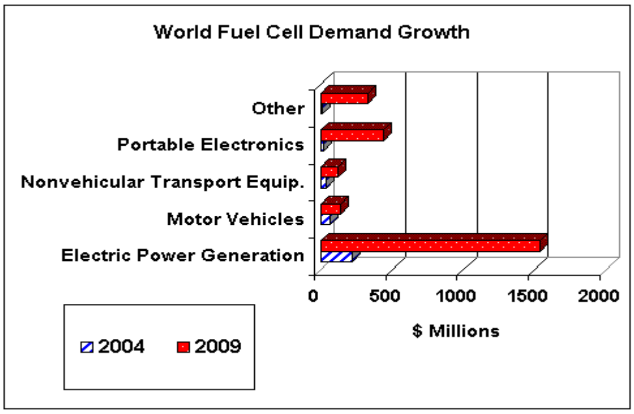

Figure 1.1: World's Fuel Cell Demand Growth from 2004-2009 (Shirley and Donald Georgi, 2005)

The characterization of fuel cells is basically differs from each other depending on the electrolyte types and the power they can generate. Due to rapid fuel cell research development internationally, there are many types of fuel cells that were developed and produced. However, there are five types of fuel cells that can be considered as the most commonly used and have high energy efficiency. The five types are:

(i) Alkaline fuel cell
(ii) Proton Exchange Membrane fuel cell
(iii) Phosphoric Acid fuel cell
(iv) Molten Carbonate fuel cell
(v) Solid Oxide fuel cell

The proton exchange membrane fuel cell received high demands especially from the transportation field due to its compact size and low operating temperature.

Sulfonation of polymers was used in creating membranes for the proton exchange membrane fuel cells as an alternative method to find possible replacements for the Nafion membrane. The identification of an economical and productive method to create a possible replacement that can overcome the drawbacks of Nafion membrane is crucial since the proton exchange membrane fuel cell needs to have a good and stable membrane to achieve high performance and energy efficiency.

1.2 Problem Statement

Nowadays, many proton exchange membrane fuel cell uses Nafion membrane which is considered as the standard membrane. However, Nafion is manufactured by DuPont only. This matter will make Nafion considered as quite hard to find. Nafion also have certain limitations. One of the major drawbacks of Nafion is it cannot operate at high temperature. It is also too dependant on the water quantity of the membrane. This research was conducted in order to get alternative polymer material for the membrane. The polymer must be low cost and can retain water at very high temperature. Finally, the newly modified polymer must be able to overcome the standard membrane (Nafion) drawbacks. Polysulfones and polyethersulfones have been recognized as the cheapest material among other engineering polymers and also available commercially.

1.3 Objective

The objective of this research was to prepare and produce mixed matrix of sulfonated polysulfone and polyethersulfone for proton exchange membrane fuel cell application.

1.4 Scope of Study

In order to achieve the objective, the following scope of study has been set:

(i) Preparation of sulfonated polysulfone by sulfonation process

(ii) Physicochemical study of the mixed matrix of sulfonated polysulfone and polyethersulfone membrane

CHAPTER II

LITERATURE REVIEW

2.1 Membrane Review

Membrane has been used in various fields in human technologies such as power generation, waste treatment, medical purposes and many more. The selective permeability nature of membrane made it very useful especially in filtration and separation process. The development of proton exchange membrane fuel cell (PEMFC) has made membrane usage in power generation became more important and crucial.

2.1.1 Definition of Membrane

The word membrane is derived from a Latin word, *membrana* which means skin. There are various definitions about membrane. In general, membrane can be defined as a selective barrier between two phases, a thin barrier that permits selective mass transport or a phase that acts as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or more species. Barrier or border is the word that can best describe membrane in short (Nunes and Peinemann, 2001).

2.1.2 Membrane Separation Process

Membrane uses separation process as its mode of operation. The basic membrane separation process is shown in Figure 2.1.

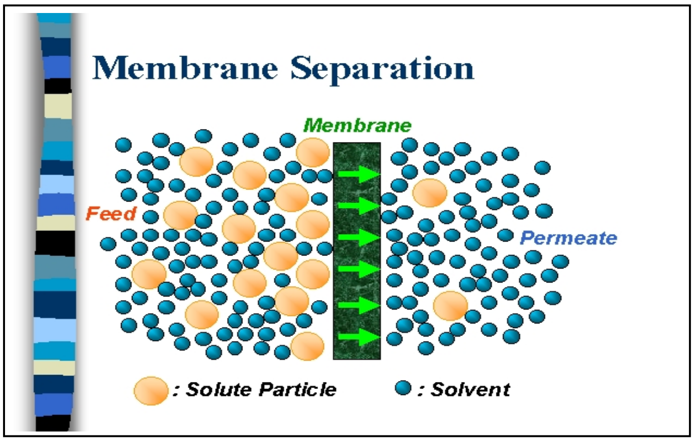

Figure 2.1: Basic Membrane Separation Process (Stookey, 2001)

Membrane separation processes can be separated into several categories and applications. The application of membrane separation process in industrial and commercial field has been expanding since the early discovery of membranes. The Germans are one of the earliest people who used membrane technology in their industries in 1920 followed by the Dutch and the Americans in 1950 and 1955 (Stookey, 2001).

2.1.3 Membrane Materials

Material selection in constructing a membrane is crucial as it determines the membrane performance. Several criteria that need to be considered in choosing membrane materials are:

(i) Material availability
(ii) Chemical stability
(iii) Easy formation
(iv) Approval of food and water contact

Table 2.1 showed the membrane materials and its descriptions.

Table 2.1: Membrane Materials

Membrane Materials	**Descriptions**
Polymer	Polysulfone, polyethersulfone, cellulose acetate and polyamide thin film
Ceramic	Available in microfiltration and ultrafiltration format,great tolerance to acids and alkalis, long life and perceived robustness
Glass	Hollow fiber form, pore size: 10-90 nm and used in biotech industries
Steel	Made from sintered stainless steel, available in tubes, robust, suitable for aggressive environments but not suitable for microfiltration due to large pore size

Polymers have been considered as the most suitable material for the proton exchange membrane fuel cell due to its ability to separate ions and act as a solid electrolyte for the fuel cell. Although interest in synthesizing polymers for different applications has been observed for about a century, major developments in this field were made only in the recent past.

2.1.4 Types of Membranes

Membranes are classified into several types according to its functions. Mainly, membranes are divided into 2 categories which are biological and non biological membranes. Biological membranes are the membrane that naturally constructed and usually situated in the body of a living things like humans and animals. Some examples of biological membranes are:

(i) Cell membrane- a selectively permeable lipid bilayer found in all cells. It contains primarily proteins and lipids.

(ii) Mucous membrane- situated at several places continuous with skin such as nostrils, genital areas, lips, ears and the anus.

(iii) Organelle membranes- divided into two; outer and inner. The outer membrane refers to the outside membrane of the Gram-negative bacteria, the mitochondria or the chloroplast. The inner membrane is the biological membrane of an organelle or a Gram-negative bacteria that is within an outer membrane (Baker, 2001).

The non biological membranes are the membranes that constructed artificially or mechanically. It can also refer to some materials that have the characteristics to become a membrane. Examples of non biological membranes are:

(i) Artificial membrane- prepared for separation tasks in laboratory or industry. Typical usages in industries are water purification and desalination, dehydrogenation of natural gas and as a component in fuel cell. An example for this is ion exchange membrane which is made from ion exchange resins.

(ii) Semipermeable membrane- allows selective molecules or ions to pass it by diffusion. An example of this is the thin film on the inside of an egg.

2.1.5 Ion Exchange Membrane

The core of the ion exchange membrane manufacturing is the preparation of the ion exchange resin. An ion exchange resin is an insoluble matrix (or support structure) normally in the form of small (1-2 mm diameter) beads, usually white or yellowish, fabricated from an organic polymer substrate. The material has highly developed structure of pores on the surface of which are sites with easily trapped and released ions. The trapping of ions takes place only with simultaneous releasing of other ions; thus the process is called ion exchange. There are multiple different types of ion exchange resin which are fabricated to selectively prefer one or several different types of ions. Besides being made as bead-shaped materials, ion exchange resins are produced as membranes. The membranes made of highly cross-linked ion exchange resins that allow passage of ions but not of water are used for electrodialysis. The ion exchange resins are divided into four major groups according to their functional groups:

(i) strongly acidic (typically, sulfonic acid groups such as sodium polystyrene sulfonate or polyAMPS)
(ii) strongly basic, (quaternary amino groups, for example, trimethylammonium groups like polyAPTAC)
(iii) weakly acidic (mostly, carboxylic acid groups)
(iv) weakly basic (primary, secondary, and/or ternary amino groups, such as polyethylene amine)

Ion exchange membrane is the major component in a proton exchange membrane fuel cell where it acts as the separator of the fuel molecule (mostly hydrogen). The membrane will let only the protons from the hydrogen molecules to permeate pass it and the electrons will forced to travel through an external circuit, creating a current flow around the fuel cell. The standard membrane used in proton exchange membrane fuel cell nowadays is Nafion, manufactured by DuPont. However, Nafion has several limitations in its operation such as inability to function in high temperatures (above 80-100ºC) and high dependency on water level. One of the characteristics of Nafion is selectively and highly permeable to water. Greater degree of hydration of the Nafion membrane will lower the ion permittivity. Since water is a byproduct of the fuel cell process, this limits the utility for Nafion for proton exchange membrane fuel cells.

2.2 Fuel Cell Review

Fuel cell is best defined as an electrochemical conversion device that produces power from the reaction between fuel and oxidant in the presence of electrolyte. The fuel cell also contains electrode, anode (negative) and cathode (positive) where the reaction takes place. The electrolyte functions as a carrier for electrically charged particles from one electrode to another and catalyst to speed up the reaction at the electrodes. Fuel cell is quite similar with dry cell because neither has any moving parts and thus minimal maintenance required. The difference between fuel cell and dry cell is that fuel cell can continuously operate as long as the fuel is supplied with the oxidant whilst dry cell must be replaced or recharged when used up. Figure 2.1 shows the basic operating diagram for a proton exchange membrane fuel cell.